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FINAL REPORT

PETROLEUM COKE GASIFICATION
IN A PLASMA REACTOR

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EXECUTIVE SUMMARY

An investigation was carried out of the gasification of fluid bed petroleum coke using a plasma spouted bed reactor. The work progressed in three distinct stages devoted respectively to the design and testing of a magnetically rotated plasma torch for operation with pure hydrogen over the power level of 10-30 kW, the development and the determination of the characteristics of the plasma spouted bed reactor, and finally, the testing of the petroleum coke gasification in an Ar/H₂.

While considerable success was achieved in the first two stages of the study, the final results of the coke gasification experiments were less than satisfactory since little gaseous hydrocarbons could be detected at the exit of the reactor. This could be, in part, due to the lack of appropriate quench of the reaction products, although the main reason is essentially the particularly low volatile matter content of the petroleum coke used in the first place.

Based on the results of the present investigation, it is unlikely that further work on the gasification of the petroleum coke in a hydrogen plasma could be successful. A number of interesting alternatives, however, are possible and worthy of investigation such as the production of syngas (CO/H₂) through the reaction of water vapour with the petroleum coke in the plasma spouted bed reactor, or the use of this same type of reactor for complete combustion of the petroleum coke.

ACKNOWLEDGMENT

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Special thanks are also due to Dr. Keith Belinko of Petro-Canada, Calgary office and Dr. Colin Hamer of Energy Mines and Resources Canada, Ottawa, for their help in obtaining the samples of the fluid bed petroleum coke used in this investigation.

WORK GROUP

This project required a team effort in which the following persons participated in the different stages of its development.

Professor Maher I. Boulos	Project coordination.
Dr Jerzy Jurewicz	Research associate; Responsible for the development of the magnetically rotated plasma torch and the design and testing of the reactor system.
Mr. Pierre Proulx	Ph.D. student; Carried out experimental study and theoretical analysis of the flow and temperature fields in the spouted bed reactor.
Mr. Jean-Serge Gagnon	Laboratory technician; Helped in the setting up of the experimental facility and the preliminary tests.
Mr. Michel Trottier	Laboratory technician; Carried out the chemical characterization of the petroleum coke used.

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1. Introduction

Over the last forty years there has been a sustained interest in the processing of hydrocarbons under plasma conditions. In fact one of the first large scale industrial application of plasma technology is that of Chemische Werk Hüls in West Germany (1) where acetylene has been produced since the early forties through the cracking of natural gas in an arc reactor. Hüls' present production capacity is estimated to be 120 000 tons C_2H_2 per year, with an annual energy consumption of 1.5 million MW-h.

Studies have also been carried out, with varying success, of the gasification of heavy oils (2,3), wood (4), peat (5) and coal (6,7) using plasma technology. In most of these applications, the plasma has been essentially used as high energy source rather than as a source of chemical species. The transformations taking place in the case of coal gasification, for example, is one of flash devolatilization of the volatile matter content of the coal followed by the thermal cracking of the hydrocarbons in the gaseous phase in order to obtain lower molecular weight hydrocarbons. The processes had to be interrupted by proper quenching techniques in order to avoid the excessive formation of soot. In the Avco process for coal gasification, which was tested at a level of 1 MW, the reaction products contained a mixture of hydrogen, acetylene, ethylene, CO and CO_2 . A water quench was noted to favor the formation of more acetylene, CO and CO_2 while a hydrocarbon quench produced a richer mixture of acetylene and ethylene. According to Avco, the specific energy requirement for the hydrocarbon quench process was estimated to be 4.8 kW-h/lb C_2H_2 or 2.8 kWh/lb of a mixture of C_2H_2 and C_2H_4 .

In the present study, a specific effort was devoted to the testing of the possibility of the gasification of carbonaceous material through the direct chemical reaction between the carbon, in solid form, and a hydrogen plasma. The source of carbon used in this case was Canadian petroleum coke obtained through the fluid bed

coking processes. Such a feed stock had the following characteristics which made it distinctly different from other feed stocks used in earlier gasification studies.

1. Low volatile matter content. Since the petroleum coke is already a by-product of the high temperature coking of heavy oils, its volatile matter content is as low as 5-6% by weight compared to 35-38% in the coal used by Hüls (1) and Avco (6).
2. High sulphur content. In the range of 4 to 6% by weight.
3. High ash content. In the range of 6-7% by weight.

The approach used was essentially experimental based on the development of an appropriate reactor system for the contacting of the petroleum coke with a pure hydrogen plasma. Two types of reactors were considered in the early stages of the project. These are:

- The dilute-phase reactor, in which the coke particles are injected into a d.c. plasma jet. In this case the expected residence time of the particles in the plasma would be limited to a few milliseconds depending on the operating conditions used.
- The dense-phase reactor in which the plasma jet is injected into a bed of petroleum coke powder. Relatively little was known about the stability and the operating characteristics of this type of plasma reactor. It offered, however, the principal advantages of long residence time, repeated exposure of the particles to the plasma, and high energy efficiency.

While the initial proposal was based on the testing, in the first place, of a dilute phase type of reactor, preliminary experiment with a dense phase reactor were sufficiently encouraging to justify proceeding directly to the development and testing of the plasma spouted bed reactor for the process under consideration.

Since a key part of the proposed approach required the contacting of the petroleum coke with a pure hydrogen plasma under atmospheric pressure or soft vacuum conditions, it was necessary to test appropriate d.c. torch designs in order to optimize the performance of the plasma torch under these conditions.

Throughout its two-year period, this project went through the following stages of development.

- Design modifications and testing of the d.c. plasma torch for optimal operation with pure hydrogen as the plasma gas.
- Development and testing of the plasma spouted bed reactor. This stage of the work was carried out essentially with a non-reacting system.
- Petroleum coke gasification. This includes the characterization of the petroleum coke to be used, the development of chemical analysis technique for the determination of the gas phase chemical composition and the preliminary gasification experiments.

2. The magnetically rotated d.c. plasma torch (MRP-torch)

2.1 Introduction

One of the first tasks in this project was to modify our standard d.c. plasma torch design in order to be able to operate it with pure hydrogen as the plasma gas at near optimal energy efficiency. Specific changes in the anode design were also tested in order to reduce, if possible, the velocity of the plasma gas at the exit of the torch. This would result in the increase of the contact between the plasma and the coke particles as well as favour a more stable spouting of the reactor.

The approach adopted involved the addition of magnetic field rotation of the anode arc root to our standard torch design. This was followed by the construction of a revised torch design incorporating magnetic arc rotation, identified as the magnetically rotating plasma torch (MRP-torch), which was used in the subsequent part of this study. In this section a brief description of the principle feature of the torch design tested are given together with typical performance data.

2.2 The standard d.c. torch design

A schematic of one of the standard d.c. torch design used is given in Figure 2.1. This is based on the use of a thoriated tungsten cathode and a water-cooled copper anode. The gas distribution in the annular space between the cathode and the anode was achieved using a ceramic diffuser ring identified as a cross hatched part in the drawing. Included in this Figure are details of two of the tested anode designs as well as the relative dimensions and position of a 510-turn magnetic coil which was placed around the anode region to achieve a better control of the position of the arc root and its rotation.

Preliminary experiments, unfortunately, showed the front O-ring around the anode to be exposed to excessive heating which reduced considerably its lifetime; a minor modification of the anode design, as shown in Figure 2.2, took care of this problem.

The torch was then subjected to systematic calorimetric study using a cup-type calorimeter. The parameters investigated were:

- The anode channel dimensions, diameter, d , and length, L_a . The latter was measured between the cathode tip and the down-stream edge of the anode.
- The magnetic field intensity, B_z , and its direction. A "N" magnetic field was one in which the field was directed towards the torch, while for a "S" field, the line of force were directed away from the torch.
- Location of the center of the magnetic field coil with respect to the anode as shown in the top part of Figure 2.2. This was identified by the distance, L_c , measured between the cathode tip and the center of the coil.
- Plasma gas composition and flow rate.

2.3 Typical results

Typical results are given in Tables 2.1-2.9. These show the effect of increasing the plasma gas flow rate, for the same power setting (approximately 20 kW), on both the current and voltage characteristics of the torch, its energy efficiency as well as the specific enthalpy of gas at the exit of the torch, kW-h/m³(STP). The energy efficiency, η , was defined as the ratio of the energy in the plasma gas at the exit of the torch to the total electrical energy dissipated in the torch.

The plasma gas used was pure hydrogen at atmospheric pressure. The current in the 510-turn magnetic field coil was kept constant at 10 A giving rise to a maximum magnetic field intensity in the center of the coil of 3162 Gauss.

It may be noted from Table 2.1 that increasing the plasma gas flow rate resulted in a considerable increase of the torch efficiency from 29.9% at 23.3 l/min to 59.5% at 70.0 l/min. The increase of the energy in the plasma gas at the exit of the torch, however, was not sufficient to compensate for the increased volume of the gas going through the torch. This resulted in a slight reduction of specific enthalpy of the plasma at the exit of the torch from 4.5 to 2.71 kW-h/m³. The same effect is systematically observed for different operating conditions (Tables 2.2-2.7).

From a comparison of the data given in Table 2.2 with those of Table 2.1, it may be noted that the direction of the magnetic field polarity has a significant influence on the torch performance. A reversal of the field polarity from N, in Table 2.1 to, S, in Table 2.2, results in an increase of the energy efficiency of the torch and consequently the specific enthalpy of the plasma at the exit of the torch.

In Tables 2.3 and 2.4 data are reported for two other anode diameters, 5.16 and 7.8 mm respectively. It may be noted that, over the range investigated, changes in the anode diameter had relatively little effect on the energy efficiency of the torch.

Further testing was carried out using the 7.8 mm anode with a, S, type magnetic field. The results given in Tables 2.5-2.7 aim at identifying the effect variation of length of the anode channel and the relative position of the magnetic field coil on the energy efficiency of the torch.

From a comparison of the data given in Table 2.6 with that of 2.5, it is obvious that, provided the torch operation remained stable, reducing the length of the anode from 29 mm to 21.5 mm resulted in an increase of the energy efficiency by almost 10%. Moving the magnetic field coil center further downstream, from 9.0 to 19.5, Tables 2.6 and 2.7, results in a further increase of the energy efficiency of the torch specially at low plasma gas flow rates.

The highest energy efficiency obtained using our standard plasma torch was 70%.

2.4 The magnetically rotated plasma torch (MRP-torch)

Based on the results of the previous experiments, a new design of an MRP-torch was developed as shown in Figure 2.3. The anode diameter in this case was maintain at about 6.0 mm and the length of the anode channel slightly reduced to 13 or 18 mm. The core of the magnetic field coil, however, was brought in much closer to the anode as shown in Figure 2.3. A photograph of the MRP plasma torch is given in Figure 2.4.

The gas injection in the discharge chamber was also modified compared to our standard torch design, incorporating a strong swirling flow component which added to the rotation of the anode are root thus improving the stability of the plasma and reducing electrode wear.

Calorimetric evaluation of the MRP-torch design revealed excellent performance which surpassed our design objections reaching as high as 94% in some cases. A summary of typical operating conditions, the energy efficiencies, and the plasma specific enthalpy obtained using this torch with a mixture of argon and hydrogen as the plasma gas is given in Table 2.8.

Table 2.1 Performance data of the standard d.c. plasma torch with magnetic rotation of the arc root

Anode diameter = 7 mm Coil current = 10 A Magnetic field = N L_a = 29.0 mm L_c = 9.0 mm					
Gas flow rate (l/min)	23.3	32.8	46.8	56.2	70.0
Current (A)	195	180	160	160	150
Voltage (V)	108	113	121	126	128
Power (kW)	21.1	20.3	19.4	20.2	19.2
Efficiency, η (%)	29.9	38.7	51.0	55.4	59.5
Sp Enthalpy (kWh/m ³)	4.50	3.99	3.51	3.31	2.71

Table 2.2 Performance data of the standard d.c. plasma torch with magnetic rotation of the arc root

Anode diameter = 7 mm Coil current = 10 A Magnetic field = S L_a = 29.0 mm L_c = 9.0 mm					
Gas flow rate (l/min)	23.3	32.8	46.8	56.2	70.0
Current (A)	200	180	160	150	140
Voltage (V)	112	121	130	136	141
Power (kW)	22.4	21.7	20.8	20.4	19.7
Efficiency (%)	35.0	43.4	54.6	61.2	64.8
Sp Enthalpy (kWh/m ³)	5.60	4.80	4.04	3.70	3.04

Table 2.3 Performance data of the standard d.c. plasma torch with magnetic rotation of the arc root

Anode diameter = 5.16 mm Coil current = 10 A Magnetic field = N L_a = 29.0 mm L_c = 9.0 mm					
Gas flow rate (l/min)	23.3		46.8		70.0
Current (A)	220		180		160
Voltage (V)	94		100		111
Power (kW)	20.7		18.0		17.8
Efficiency, η (%)	29.5		41.0		54.6
Sp Enthalpy (kWh/m ³)	4.36	—	2.63		2.30

Table 2.4 Performance data of the standard d.c. plasma torch with magnetic rotation of the arc root

Anode diameter = 7.8 mm Coil current = 10 A Magnetic field = N L_a = 29.0 mm L_c = 9.0 mm					
Gas flow rate (l/min)	23.3	32.8	46.8	56.2	70.0
Current (A)	180	170	158	140	140
Voltage (V)	123	124	132	139	144
Power (kW)	22.1	21.1	20.9	19.5	20.2
Efficiency (%)	27.5	36.0	47.2	49.4	56.5
Sp Enthalpy (kWh/m ³)	4.35	3.86	3.50	2.85	2.76

Table 2.5 Performance data of the standard d.c. plasma torch with magnetic rotation of the arc root

Anode diameter = 7.8 mm Coil current = 10 A Magnetic field = S L_a = 29.0 mm L_c = 9.0 mm					
Gas flow rate (l/min)	23.3	32.8	46.8	56.2	70.0
Current (A)	210	190	170	150	140
Voltage (V)	111	108	120	130	138
Power (kW)	22.7	22.8	22.1	20.7	20.4
Efficiency, η (%)	24.3	36.4	48.9	50.6	58.9
Sp Enthalpy (kWh/m ³)	3.93	4.21	3.85	3.11	2.80

Table 2.6 Performance data of the standard d.c. plasma torch with magnetic rotation of the arc root

Anode diameter = 7.8 mm Coil current = 10 A Magnetic field = S L_a = 21.5 mm L_c = 9.0 mm					
Gas flow rate (l/min)	23.3	32.8	46.8	56.2	70.0
Current (A)	230	180	160	140	115
Voltage (V)	108	123	139	149	166
Power (kW)	24.8	22.1	22.2	20.9	19.1
Efficiency (%)	39.5	43.0	60.3	63.8	68.6
Sp Enthalpy (kWh/m ³)	7.00	4.83	4.77	3.95	3.11

Table 2.7 Performance data of the standard d.c. plasma torch with magnetic rotation of the arc root

Anode diameter = 7.8 mm Coil current = 10 A Magnetic field = S L_a = 21.5 mm L_c = 19.5 mm					
Gas flow rate (l/min)		32.8	46.8	56.2	70.0
Current (A)		170	150	140	125
Voltage (V)		131	140	149	159
Power (kW)		22.3	21.0	20.9	19.9
Efficiency, η (%)		53.6	60.0	65.9	70.4
Sp Enthalpy (kWh/m ³)		6.06	4.48	4.08	3.32

Table 2.8 Typical performance data of the MRP-torch

Gas flow rate (l/min)						
Ar	9.3	9.3	9.3	16.0	33.0	35.0
H ₂	32.0	32.0	32.0	33.0	33.0	13.0
Coil current (A)	20.0	20.0	20.0	20.0	20.0	20.0
Power (kW)	17.0	20.0	22.0	15.0	11.0	11.0
Efficiency, η (%)	90.0	93.0	92.0	93.0	94.0	84.0
Sp Enthalpy (kWh/m ³)	6.17	7.51	8.17	4.74	2.61	3.21

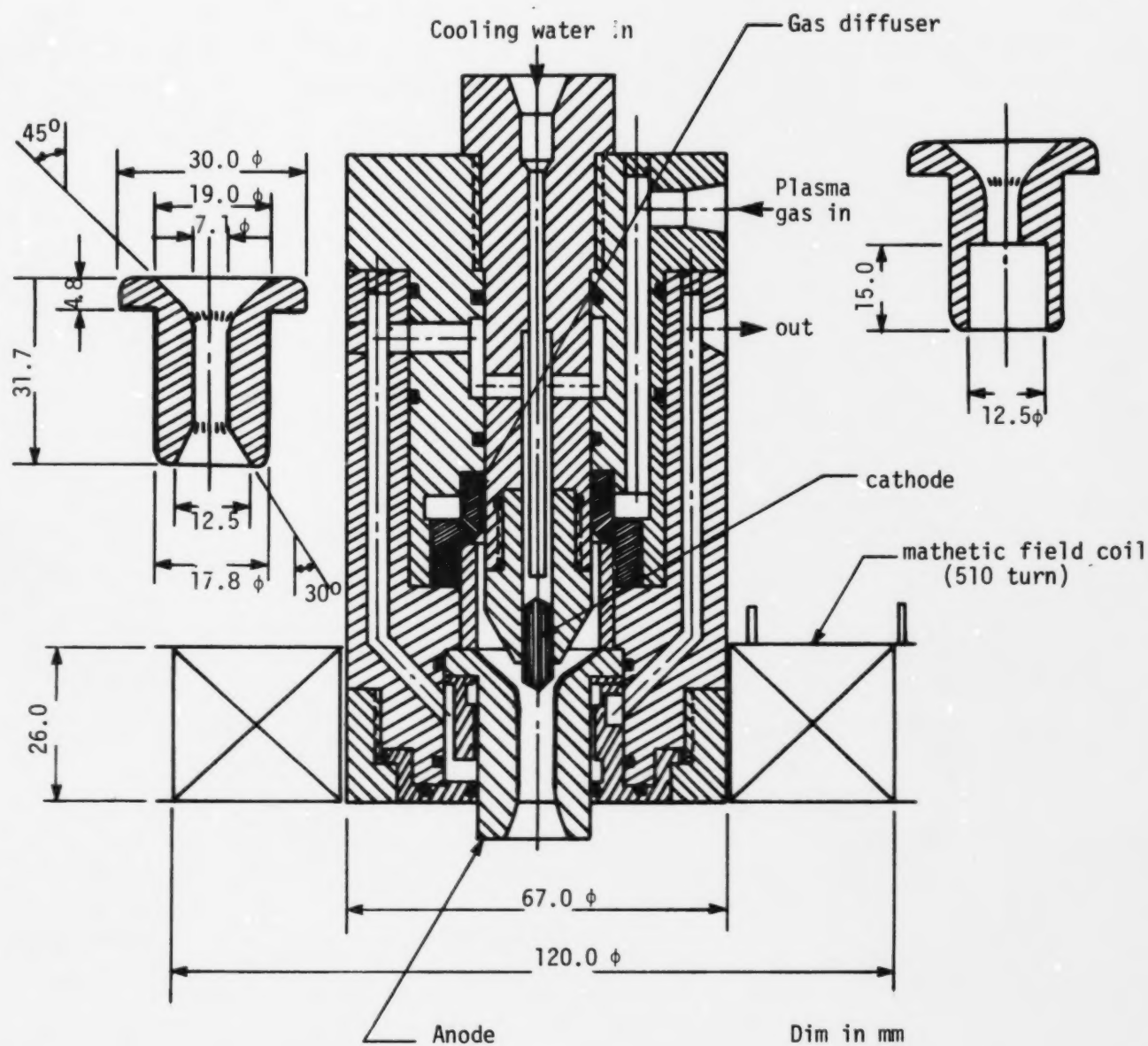


Figure 2.1 Schematic of a standard d.c. torch design including details of two of the tested anode configurations as well as the dimensions and position of the magnetic field coil

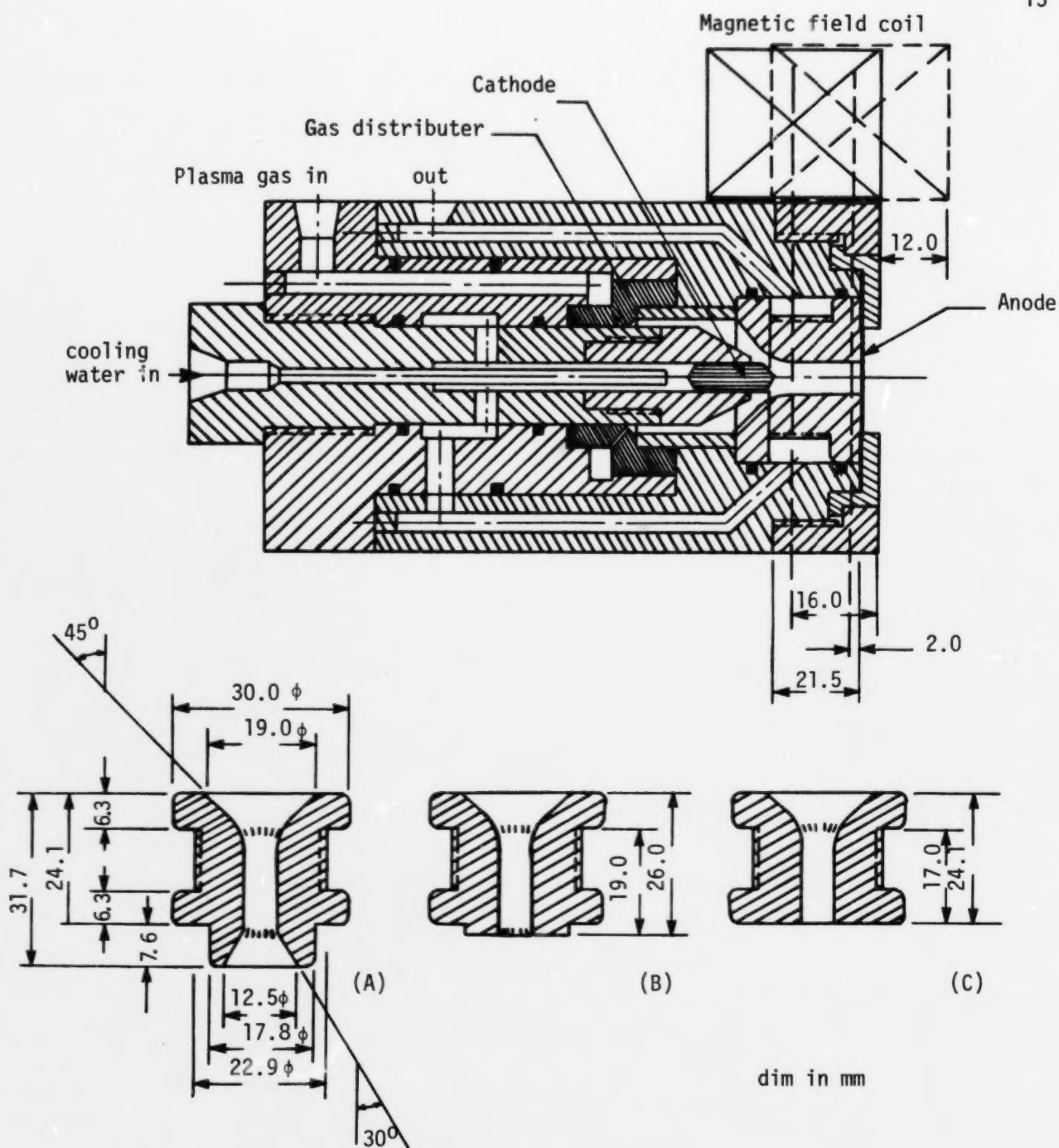


Figure 2.2 Schematic of the modified d.c. torch design.
The top part of the figure shows the relation position
of the magnetic field coil used

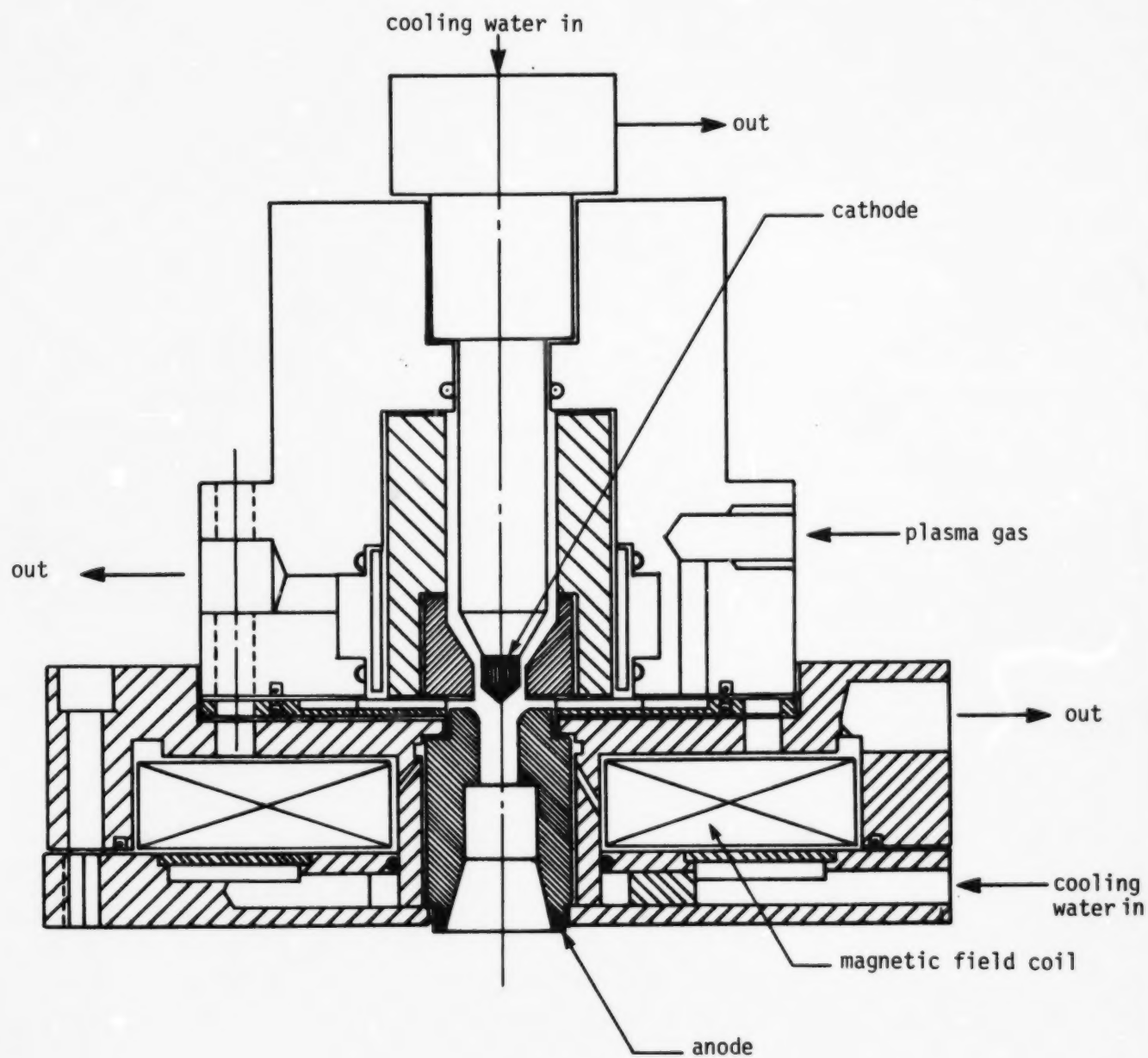


Figure 2.3 Schematic of the final version of the magnetically rotated plasma torch (MRP-torch)

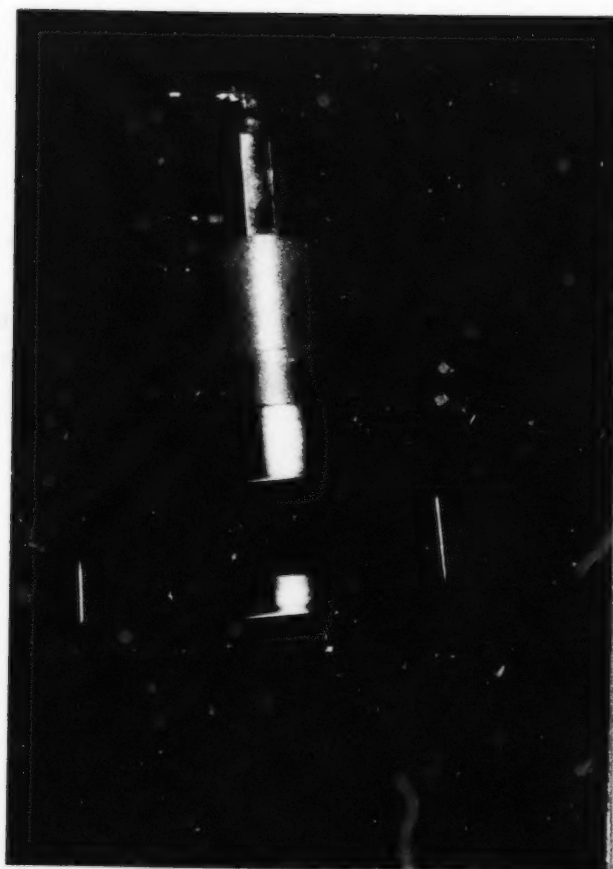


Figure 2.4 Photograph of the MRP plasma torch

3. The plasma spouted bed reactor

3.1 Basic concept

As shown schematically on Figure 3.1, the basic principal of the plasma spouted bed reactor is essentially similar to that of a standard spouted bed reactor (8). The main difference lies in the fact that the spouting gas is substituted by a d.c. plasma jet which discharges in the conical bottom of the reactor. This offers the main advantage that the radiative and convective losses from the plasma are recuperated by the solid charge of the reactor thus giving rise to substantially higher energy efficiencies. It is interesting to note that while an essentially similar type of reactor has been used in Poland in the early seventies (9,10) for coal gasification work, very little attention has been given ever since to the study of its operating characteristics and the basic phenomena involved.

It is essentially to this end that the present stage for this investigation has been conducted with the objective of obtaining basic information and design data about such phenomena as spouting stability, particle attrition and elutriation from the bed as well as particle recirculation rates.

3.2 The experimental setup

A schematic diagram of an experimental reactor used in the first stages of this study is given in Figure 3.2. This consisted essentially of a cylindrical pyrex tube, 168 mm i.d. and approximately 1 m long. The smaller diameter of the latter section was connected through a short cylindrical pyrex tube, 70 mm, i.d. to a water-cooled conical brass adaptor which incorporated the anode part of a d.c. plasma torch of standard design. The anode nozzle had an internal diameter of 7.3 mm. A 140 mm diameter stainless steel deflector, placed axially in the reactor at approximately 500 mm from the nozzle of the

plasma jet served to intercept the particles ejected from the bed.

Temperature measurements were carried out using a radiation pyrometer focussed on the interface of the bed and wall of the pyrex reactor at different levels. In a few experiments, chromel-alumel thermocouples were used. These were inserted into the bed from the side of the reactor at two levels. The first in the pyrex conical section as shown in Figure 3.2, while the second was in the brass conical section a few millimeter away from the plasma torch. In a few experiments, a radiation pyrometer was used to measure the temperature of the bed and/or wall of the pyrex tube.

3.3 Experimental procedure

For simplicity, most of the preliminary experiments were carried out using different alumina powders of particle size distributions of $53 < d_p < 106 \mu\text{m}$, $595 < d_p < 710 \mu\text{m}$ and $500 < d_p < 1000 \mu\text{m}$. The plasma torch was operated with either pure argon 47.0 l/min, or an argon/nitrogen mixture, 37.3 l/min, with 38% N_2 , by volume. The corresponding power levels varied between 9.0 to 28.0 kW respectively.

Due to the lack of cooling of the pyrex reactor wall, all experiments were carried out under transient conditions with a duration of each experiment limited to 5 to 10 min to avoid overheating of the reactor tube wall. Photographs of the reactor at different stages of its operation are given in Figure 3.3.

3.4 Results and discussion

a) Reactor stability

The first series of experiments were conducted to obtain

information about the different operating regimes of the reactor as function of the reactor loading, or height of the particle bed. This was carried out by incremental addition of different amounts of powder to the reactor, after plasma ignition, and visual observation of the behaviour of the bed. A schematic representation of the spouted bed with different particles loading, 700-2100 g of alumina, is shown on Figure 3.4.

It may be noted that at low powder loading, up to 1200 g the luminous plasma core was visible at the bed surface. With the further increase of the bed loading up to 2100 g, the plasma core was completely immersed into the bed. The latter, however, was well fluidized with a high rate of powder recirculation. Beyond a bed loading of 2100 g, the bed became increasingly unstable with visible bubbling and slugging.

b) Bed temperature profile

While most of the experiments were obviously limited to the transient heating of the bed material, it is interesting to examine the bed temperature profile which results from the balance between the heat flux from the plasma to the bed and, radiation and convective losses from the reactor wall. Typical bed temperature profiles obtained with different alumina powders and plasma operating conditions are summarized in Table 3.1. Most temperature measurements in this case were obtained using the radiation pyrometer, with the exception of the values indicated by an asterisk which were thermocouple measurements.

It may be noted that, with the exception of the region in the immediate neighborhood of the water-cooled brass cone, most of the remaining volume of the bed is at a reasonably

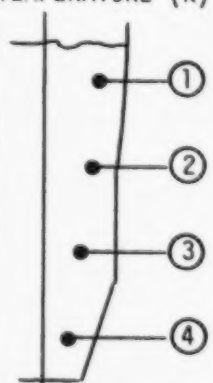
uniform temperature which can be attributed to some extent to the high level of particle recirculation in the bed.

c) Particle attrition

A special attention was given to the question of particle attrition in the bed. Samples of the bed charge were taken before and after plasma treatment and were subject to particle size analysis. Typical results given on Fig. 3.5 reveals a substantial change in the alumina particle size distribution after only a 10-minute treatment in an Ar/N₂ plasma at a power level of 28 kW.

This could be attributed to attrition due to particle-particle or particle-deflector collision or simply thermal shock of the alumina as the particles are exposed to the high plasma temperatures during their short flight in the fountain region of the spouted bed.

Table 3.1 Temperature profile for the plasma spouted bed
under different operating conditions

Al ₂ O ₃ powder	Particle size (μm)	500-1000	500-1000	500-1000	500-1000	500-1000	595-710	595-710
	Mass (g)	2160	800	1000	1500	1500	1000	1000
Plasma gases flow- rate	Argon (l/min)	47	47	47	47	47	47	23
	Nitrogen (l/min)	14	-	14	14	19	-	14
Plasma power (kW)		18.6	9.0	16.0	16.0	19.8	10.0	28.0
TEMPERATURE (K) 								
		990	890	1030	1020	1020	933*	1143*
		940						
		910						
							423	403*

* Thermocouple

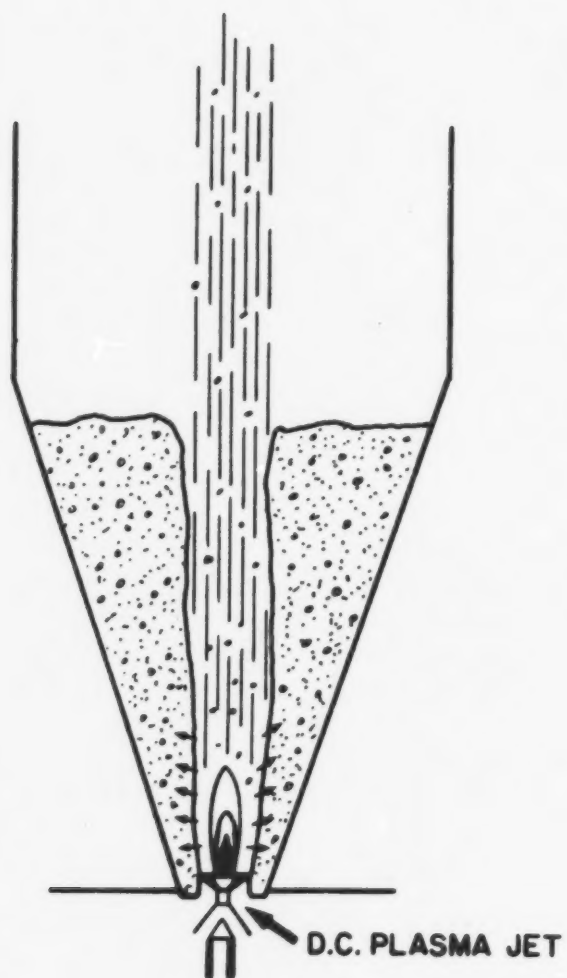


Figure 3.1 The plasma spouted bed reactor

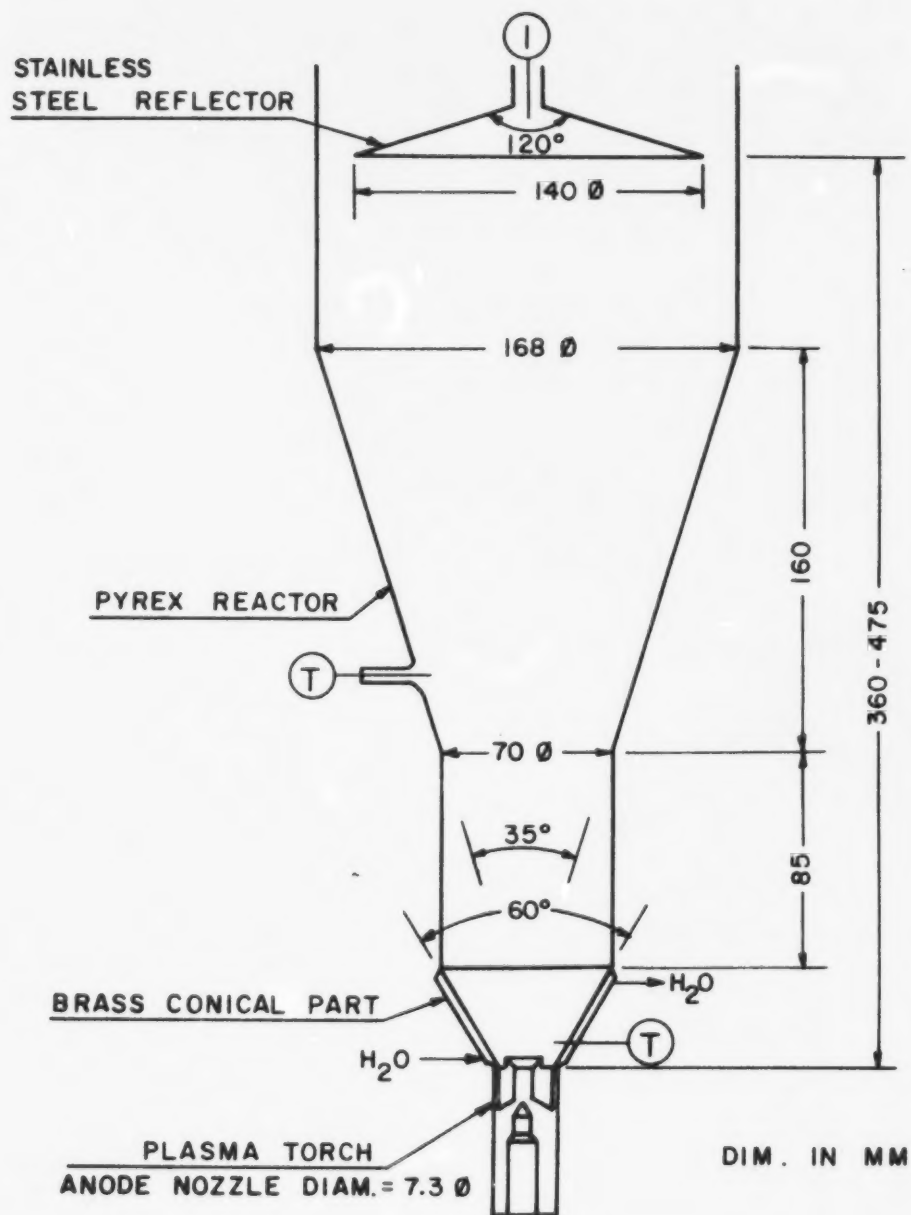


Figure 3.2 Schematic of the experimental reactor used in the preliminary testing of the spouted bed



Figure 3.3 Photographs of the spouted bed reactor at different stages of its operation

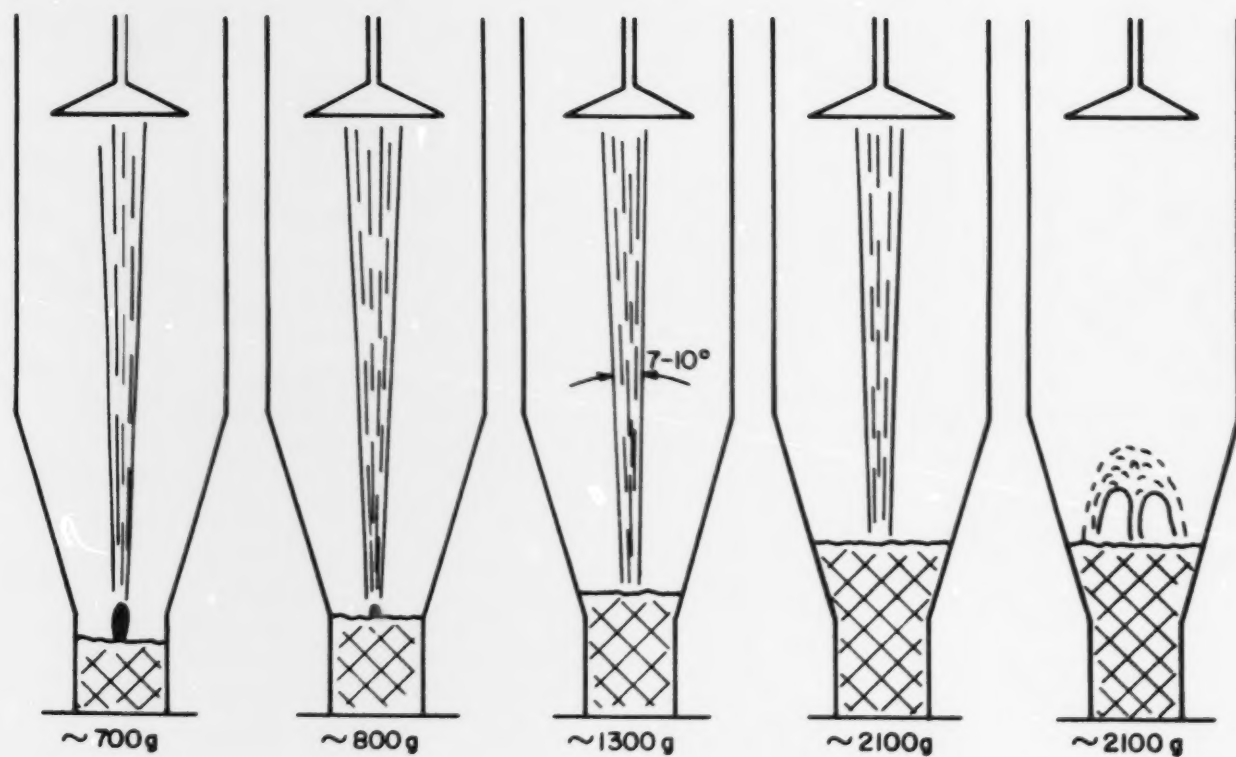


Figure 3.4 Schematic of the spouted bed with different loading of alumina powder (argon operation at 9 kW)

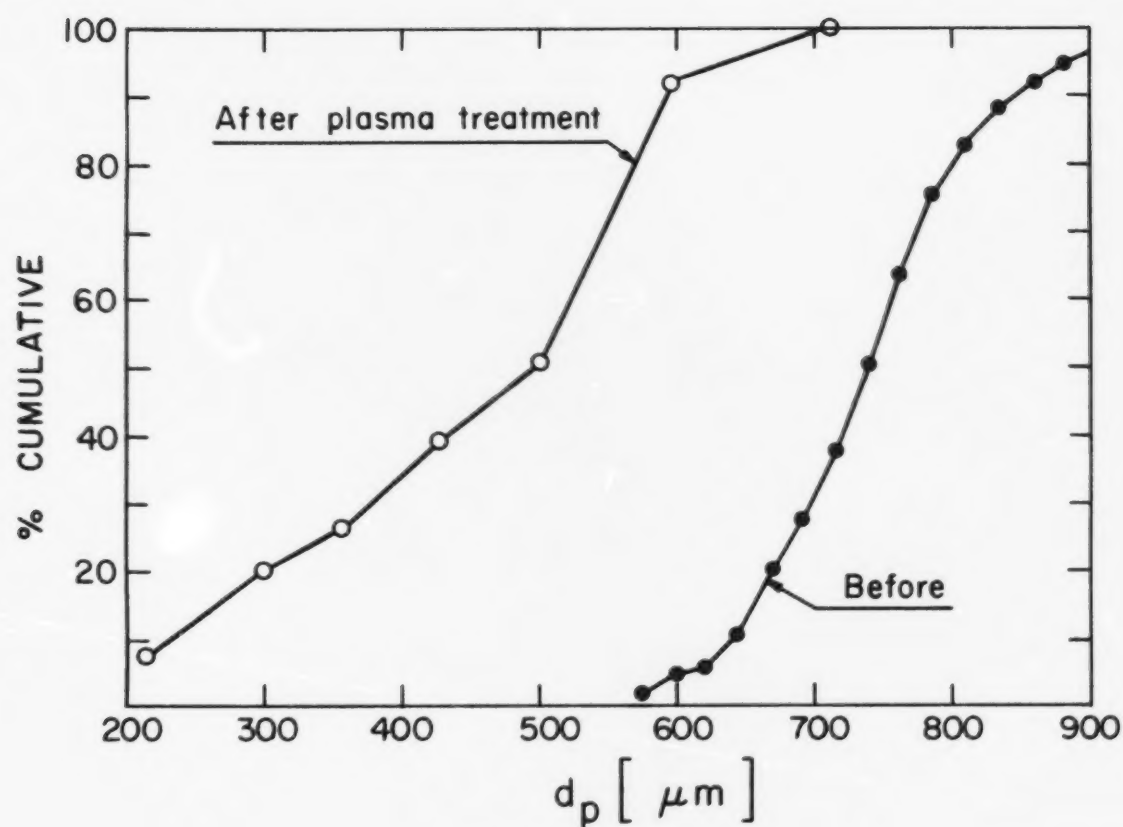


Figure 3.5 Particle size distribution of the alumina powder used in the preliminary testing, before and after treatment for 10-min in an argon/nitrogen plasma at a power level of 28 kW

4. Petroleum coke gasification

4.1 Characterization of the petroleum coke used

Both delayed petroleum coke and fluid bed coke were tested for use in this project.

The delayed coke was obtained in the form of relatively large lumps which had to be crushed and classified prior to use in the gasification reactor.

The fluid bed coke, on the other hand, was available as a powder with relatively uniform, spherical, free-flowing particles.

Most of this study was carried out using the syncrude fluid bed coke whose characteristics are summarized in this section. The coke batch used bore the number 81-17 and was taken from the Alberta plant on May 15, 1981.

4.1.1 Particle size distribution

A typical screening analysis of the fluid bed coke as received is given in Table 4.1. This had a weight median of 125-150 μm with about 14.7% of the coke being larger than 250 μm in diameter. Most of the experimental study was carried out with a relatively narrow fraction of this coke, with a particle size in the range 125-180 μm .

4.1.2 Microscopic observation

Photographs obtained using optical microscopy of typical samples for the delayed coke and the fluid bed coke are given in Figures 4.1 and 4.2 respectively. These show the delayed coke to be composed of sharp edged particles

while the fluid bed coke is composed of well rounded particles with a rather porous internal structure. A cross-section of a few of relatively large fluid bed coke particles are included in Figure 4.2 showing some details of their internal structure.

4.1.3 Chemical analysis

In order to determine whether there was any variations in the chemical composition of the different size fractions of the coke, a separate elemental analysis was carried out for each of the fractions obtained in the screen analysis. The results, included in Table 4.1 show no significant variations between the different size fractions for each of the elements measured.

Detailed elemental analysis of the fluid bed coke used in this investigation, batch 81-17, is given in Table 4.2. The analysis of a delayed coke and a suncore #2074 is also included for comparison.

A complete analysis of the syncrude coke is given in Table 4.3. This show a volatile matter, and an ash content, of less then 6% each. The sulfur content was particularly high in all of these samples and was generally about 6-7%. Particularly relevent to this study is the low level of hydrogen in this coke which was less than 1.5% by weight.

4.2 The plasma spouted bed reactor used in the gasification experiments

Based on the results of the preliminary study of the pyrex-spouted bed reactor, a stainless steel reactor was designed and

constructed. A schematic of the experimental set-up and details of the reactor design and its principal dimensions are given in Figures 4.3 and 4.4 respectively. Only the upper part of the reactor and its cover were water-cooled while the lower part was insulated using a refractory blanket. The MRP torch was connected to the bottom of the reactor while the gases left the reactor through a water-cooled side port. After passing through a cyclone collector and a high temperature filter, the gases were cooled using a double pipe heat exchanger before entering a rotary vacuum pump. Finally, at the exit of the pump, the gases were sent to an appropriate flare.

Because of the need to start the plasma torch without the powder, the reactor was mounted on a pivoting system which allowed the torch and the reactor to be kept in a horizontal position until the torch was ignited. The powder, during that time, was kept in small canister connected to the reactor through a vacuum seal. Following ignition and adjustment of the torch operating conditions to the required power level, the reactor was brought back to its normal vertical position allowing the powder to flow from the canister into the main body of the reactor.

The thermal characteristics of the reactor were determined in the first stages of its operation by running it empty at relatively low power and following the temperature history at different points of the reactor. Typical results obtained, using an Ar/N₂ plasma and for a N₂ plasma at power levels of 7 kW and 15.7 kW respectively, are given in Figure 4.5.

It is noticed that even at relatively low power, 7 kW, the temperature of the walls of the reactor as well as that of the deflector rises rather sharply in the first few minutes of

operation reaching a plateau of about 600-800°C in about 15 min. With the increase of the torch power to 15.7 kW, the reactor temperature rise is considerably steeper reaching the rather dangerous level of almost 900°C in less than 10 min.

Based on these preliminary results, it was necessary, for safety reasons, to either line the reactor walls with an appropriate refractory, or add a water-cooling jacket at least around the cylindrical section of the reactor. The last option was chosen for simplicity as well as to avoid possible contamination of the coke by the refractory material through wall abrasion.

A revised version of the experimental set-up is shown in Figure 4.6. This included the following changes:

- a) Water-cooling of the reactor wall.
- b) Introduction of a water-cooled quench probe centrally in the reactor.
- c) The addition of a load cell under the fine collection chamber of the cyclone which allowed the continuous monitoring of the elutriation rate from the reactor.
- d) The removal of the heat exchanger normally placed after the filter since it was no more needed.
- e) The addition of a second, back-up filter for extra protection of the vacuum pump from accidental powder entrainment with the flow.

A photograph of the set-up is given in Figure 4.7. For security reasons, the whole set-up was placed in a wall ventilated hood as shown in Figures 4.8 and 4.9.

4.3 Instrumentation and chemical analysis

Special emphasis was given to the proper instrumentation and the on-line computer controlled data acquisition in order to maintain a close follow up of the conditions in the different parts of the reactor system. The parameters monitored using a hp 85 computer and hp 3421 data acquisition station were:

- a) Temperature of the cooling water in and out the reactor system as well as that at different locations in the reactor system.
- b) The absolute pressure in the reactor.
- c) The weight of the powder in the cyclone collection chamber.
- d) The current intensity and the voltage across the plasma torch.

Moreover, provision were made for the periodic sampling the gas stream at the exit of the reactor for analysis, using gas chromatography, for CO, CO₂, CH₄, C₂H₂, C₂H₄. Due to the rather lengthy retention time associated with such an analysis it was necessary to use a 16-loop valve for the storage of the samples during the course of the experiment. These were later subject to detailed analysis using an hp 5880 gas chromatograph. Figures 4.10 and 4.11 give different views of the control pannel and data acquisition, as well as the gas chromatograph, respectively.

4.4 Results and discussion

Two sets of runs were carried out with the fluid bed petroleum

coke using an Ar/H₂ plasma under atmospheric pressure. A summary of the experimental conditions is given in Tables 4.4 and 4.5.

In the first five runs #21-32, Table 4.4, no quench gas was used. The experimental procedure involved the transient heating of the bed charge (about 500-1000 g) for a period of 15-20 min during which the temperature history of the reactor was followed. Samples of the gaseous products at the exit of the reactor were also taken periodically during each run for further analysis. At the end of the run, the plasma was stopped and the quantity of the powder left in the reactor and that accumulated in the cyclone collector and filter was determined. These were also subject to elemental analysis to determine their C, H, N, S, O, and ash content. The powder distribution at the end of the run as well as the elemental analysis, are given in Table 4.4.

It may be noted that generally the material balance closed within 5-10%. Almost 70-80% of the initial coke charge remained in the reactor at the end of the experiment, while 10-20% of the initial charge was elutriated and captured in the cyclone collector. Negligible amounts of the powder were found there in the filter, 0.1-0.2%.

Elemental analysis of the powder collected at different parts of the reactor system revealed a drop in the sulphur content of the coke after the plasma treatment. The hydrogen content of the powder collected in the cyclone was extremely low indicating a complete volatilization of whatever small amounts of volatile matter initially present in the coke.

The chemical analysis of the gas at the exit of the reactor was, however, rather discouraging since hardly any hydrocarbons such as CH₄ or C₂H₂ could be detected. A typical chromatogram of a sample of the gases obtained in run # 30 taken after 8 min

of operation is given in Figure 4.12. This shows only a very small peak corresponding to CH_4 and no detectable amounts of C_2H_2 . Rather unexpected however, was the presence of CO and CO_2 in non negligible quantities. The concentration of CO was noted to be particularly high during the first few minutes of the experiment after which it dropped rapidly with time.

An interesting observation, however, was the deposition of pyrolytic carbon on the upper sections of the reactor which seems to suggest the decomposition of any formed hydrocarbons on contact with hot sections of the reactor. This could indirectly explain the particularly low level of hydrocarbons in the exit gas.

Based on the above observation it was decided to incorporate gas quenching in the reactor. This was achieved by the introduction of a water-cooled stainless steel probe axially through the center of the reactor and the injection of hydrogen at ambient temperature. By proper adjustment of the level of the quench probe in the reactor it was possible to control the point at which the reaction products are quenched. Typically, this was carried out at a distance of 90-120 mm from the plasma torch.

Typical results are given in Table 4.5. These include the reactor operating conditions and the elemental analysis of the coke distributed in the different parts of the reactor in the presence of a hydrogen quench.

It may be noted that considerably less powder was elutriated from the reactor in this case. The hydrogen content was also noted to drop in the coke remaining in the reactor. No hydrogen or volatile matter was detectable in the powder collected

in the cyclone or filter. The sulfur analysis was not carried out for these powders.

Unfortunately, the situation was not much improved with regard to the hydrocarbon content of the gases at the exit of the reactor, as indicated by the typical chromatogram of a sample of the gases obtained in run #42, taken after 6 min operation, shown in Figure 4.13. This seems to reveal that the quench might not have been severe enough to stop the reversed decoposition reaction.

Faced with this result it was not justified to proceed further with more runs before a major re-examination of the project objectives. In fact while the petroleum coke gasification into gaseous hydrocarbons seems particularly difficult due to its low volatile matter content, a number of interesting avenues are possible and worth investigating such as the gasification of the coke as syngas through the reaction of water vapour with the coke, or the partial combustion of the coke which could be carried out in the same type of plasma spouted bed reactor that was developed in the context of this work.

Table 4.1 Screen analysis and chemical composition
of the fluid bed coke - batch no 81-17

Particle size range (μm)	weight fraction (%)	Carbon (%)	Hydrogen (%)	Sulfur (%)	Nitrogen (%)	Ash (%)	Oxygen (%)
dp < 75	6.0	79.20	1.36	6.19	1.80	7.1	4.34
75 - 90	4.8						
90 - 106	12.2						
106 - 125	12.8	79.41	1.35	6.39	1.80	6.5	4.55
125 - 150	16.5	79.78	1.35	6.23	1.80	5.6	5.24
150 - 180	17.2	79.17	1.32	6.04	1.65	5.4	6.42
180 - 212	6.9	80.15	1.30	6.54	1.73	5.0	5.28
212 - 250	8.9	78.99	1.25	6.62	1.73	5.3	6.11
250 - 355	11.2	80.20	1.23	6.55	1.76	2.5	7.76
355 - 425	2.7	80.21	1.17	6.72	1.82	4.3	5.78
425 - 500	0.8	80.44	1.12	5.31	1.86	6.0	5.27
	100.0						

Table 4.2. Typical elemental analysis of the fluid bed coke, delayed coke and suncore #2074 coke.

Only the fluid bed coke #81-17 was used in this investigation

Coke Element	Syncrude fluid coke sample 81-17 (%) weight	Delayed coke (%) weight	Suncore #2074 (%) weight
C	79.42	85.12	85.34
H	1.30	3.68	3.66
N	1.75	1.50	1.43
S	6.31	5.63	5.66
O (by diff.)	5.87	1.75	1.62
Ash	5.35	2.32	2.29

Table 4.3. Analysis of the syncrude coke
batch 81-17

<u>Proximate analysis</u>	<u>Air dried</u>	<u>Dry basis</u>	
Moisture	1.61	0.00	
Ash	6.57	6.68	
Volatiles	6.68	6.79	
Fixed carbon (by difference)	85.14	86.53	
	100.00	100.00	
<u>Ultimate analysis</u>			
Carbon	81.07	82.40	
Hydrogen (L59-0-18)	1.41	1.43	
Sulphur	6.85	6.96	
Nitrogen	2.09	2.12	
Ash	6.57	6.68	
Oxygen (by difference)	0.40	0.41	
	98.39	100.00	
<u>Calorific value</u>			
Calories/gm (gross)	7,172		
BTU/lb (gross)	12,910		
<u>Ash analysis</u>			
SiO ₂	44.65	MgO	1.44
Al ₂ O ₃	25.20	Na ₂ O	1.28
Fe ₂ O ₃	10.51	K ₂ O	1.86
TiO ₂	3.01	V ₂ O ₅	3.83
CaO	5.18	NiO	1.51
		LDF	1.49

Table 4.4 Operating conditions and typical results of
the petroleum coke gasification experiments
in the absence of product quench

Run Number		21	23	27	30	32
Plasma power	(kW)	10	11	11	15	15
Energy efficiency η	(%)	-	-	84	94	93
Argon flow rate	(ℓ /min)	35	33	35	33	16
Hydrogen flow rate	(ℓ /min)	6	12	13	33	33
Sp. Enthalpy of the gas	(kWh/m ³)	-	-	3.21	2.61	4.74
Initial charge of the reactor	(kg)	0.500	0.500	1.000	1.000	0.998
Powder distribution at the end of the run						
Reactor	(%)	-	-	80.6	72.0	68.2
Cyclone	(%)	-	-	12.5	20.6	20.5
Filter	(%)	-	-	0.2	0.1	0.2
Difference	(%)	-	-	6.7	7.3	11.0
Elemental analysis						
<u>Carbon</u>						
Reactor	(%)	81.97	79.54	82.15	82.10	84.03
Cyclone	(%)	86.38	86.09	86.28	86.49	87.07
Filter	(%)	-	-	87.35	81.63	84.17
<u>Hydrogen</u>						
Reactor	(%)	0.77	1.02	0.80	0.77	0.55
Cyclone	(%)	0.00	0.10	0.07	0.18	0.00
Filter	(%)	-	-	0.00	0.00	0.00
<u>Nitrogen</u>						
Reactor	(%)	1.50	1.57	1.57	1.42	1.40
Cyclone	(%)	1.07	1.02	1.14	1.13	0.89
Filter	(%)	-	-	0.69	0.74	0.73
<u>Sulfur</u>						
Reactor	(%)	5.25	5.40	5.07	5.74	4.15
Cyclone	(%)	4.26	4.71	4.69	4.99	5.58
Filter	(%)	-	-	-	-	-
<u>Oxygen</u>						
Reactor	(%)	2.41	4.82	2.85	2.29	1.74
Cyclone	(%)	0.49	1.11	0.84	0.42	1.17
Filter	(%)	-	-	-	-	-
<u>Ash</u>						
Reactor	(%)	8.10	7.65	7.56	7.68	8.13
Cyclone	(%)	7.80	6.97	6.98	6.79	7.29
Filter	(%)	-	-	7.76	13.40	12.43

Table 4.5 Operating conditions and typical results of
the petroleum coke gasification experiments
in the presence of a hydrogen quench

Run Number		36	37	38	40	42	43
Plasma power	(kW)	17	17	22	22	18	20
Energy efficiency η	(%)	87	90	90	92	88	93
Argon flow rate	(ℓ /min)	9.3	9.3	9.3	9.3	9.3	9.3
Hydrogen flow rate	(ℓ /min)	32.0	32.0	32.0	32.0	32.0	32.0
Sp. Enthalpy of the gas	(kWh/m ³)	5.97	6.17	7.99	8.17	6.39	7.51
Hydrogen quench flow rate	(ℓ /min)	150.0	150.0	150.0	200.0	200.0	200.0
Initial charge of the reactor	(kg)	1.800	1.500	1.226	1.800	1.800	1.564
Powder distribution at the end of the run							
Reactor	(%)	85.5	88.34	90.4	82.6	-	-
Cyclone	(%)	8.4	6.6	4.2	6.9	-	-
Filter	(%)	0.5	0.4	0.5	2.0	-	-
Difference	(%)	5.6	4.7	4.9	8.5	-	-
Elemental analysis							
<u>Carbon</u> Reactor	(%)	80.99	82.34	86.10	-	80.18	82.70
Cyclone	(%)	85.62	88.57	88.02	89.36	88.36	89.46
Filter	(%)	87.62	86.46	79.76	89.19	72.42	-
<u>Hydrogen</u> Reactor	(%)	1.05	0.65	0.00	-	0.84	0.48
Cyclone	(%)	0.00	0.00	0.00	0.00	0.00	0.00
Filter	(%)	0.00	0.00	0.00	0.00	0.10	-
<u>Nitrogen</u> Reactor	(%)	1.57	1.35	0.68	-	1.39	1.23
Cyclone	(%)	1.02	0.35	0.62	0.63	0.67	0.73
Filter	(%)	0.99	0.79	0.64	0.66	0.68	-

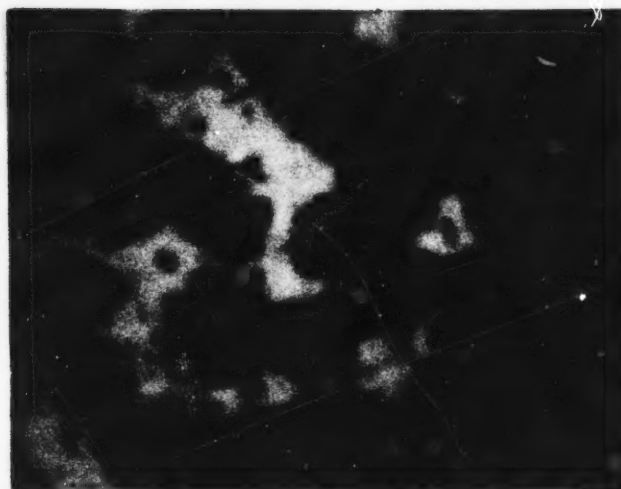


Figure 4.1 Optical micrograph of the delayed coke particles
($150 < d_p < 212$)

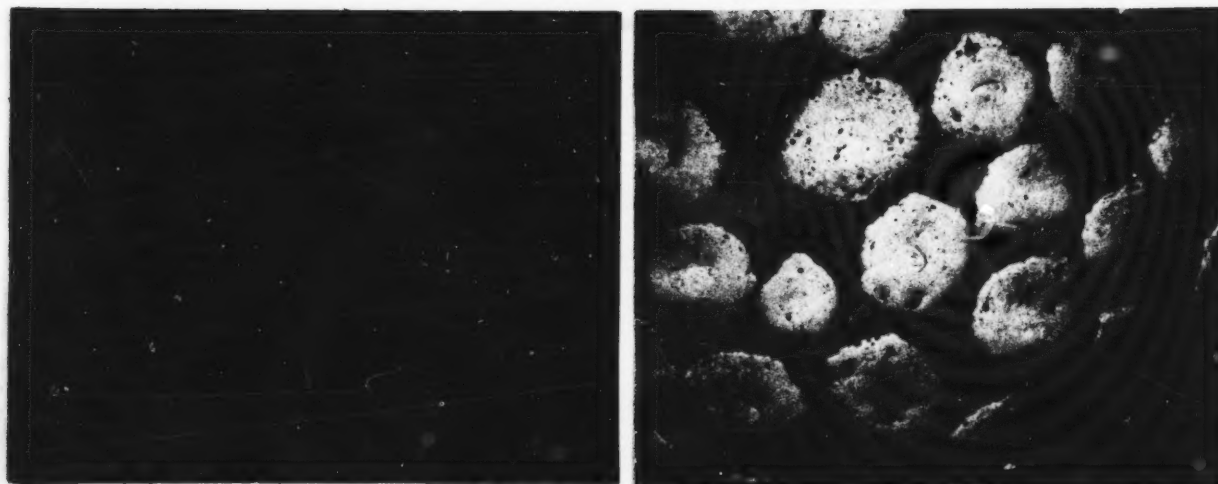


Figure 4.2 Optical micrograph of the fluid bed coke particles, Left
($212 < d_p < 355$)
The right picture gives a crosssection of the particles
($355 < d_p < 500$)

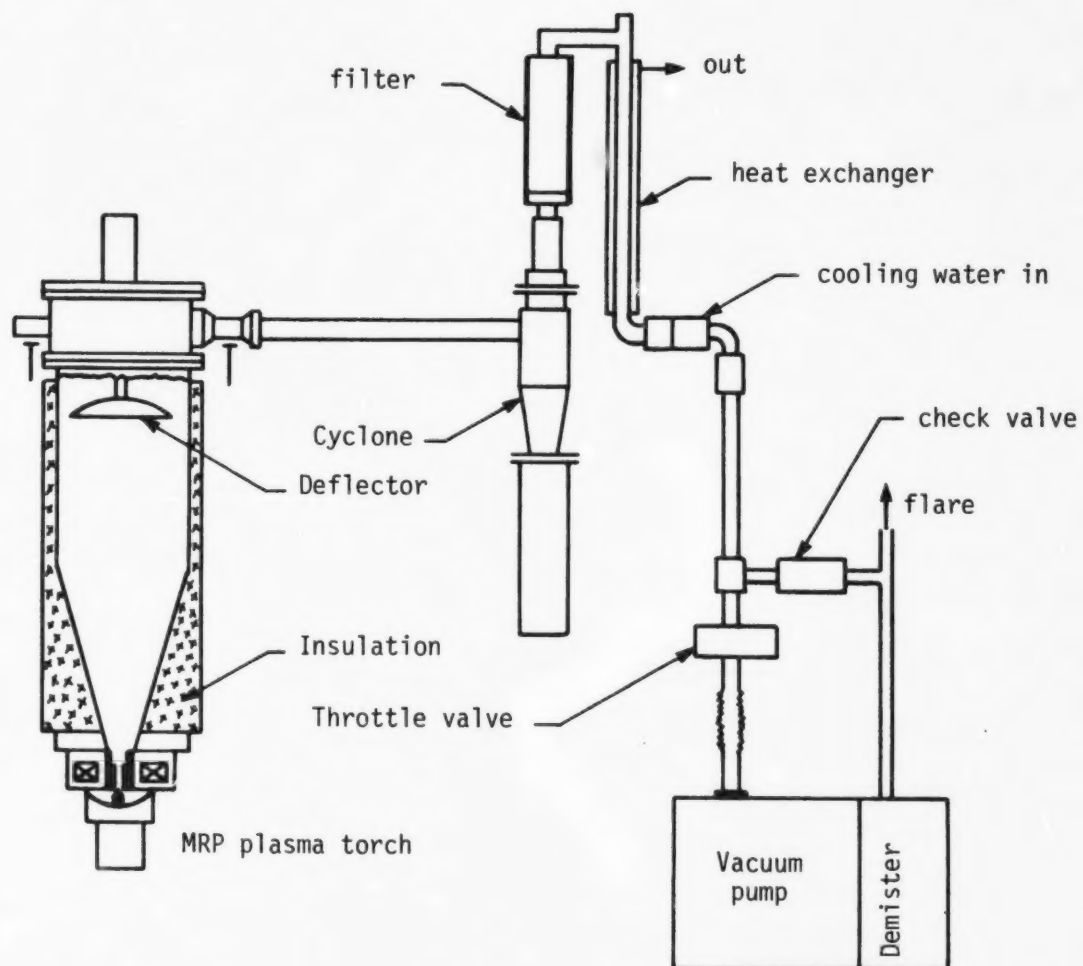


Figure 4.3 The experimental set-up including the hot-wall spouted bed reactor

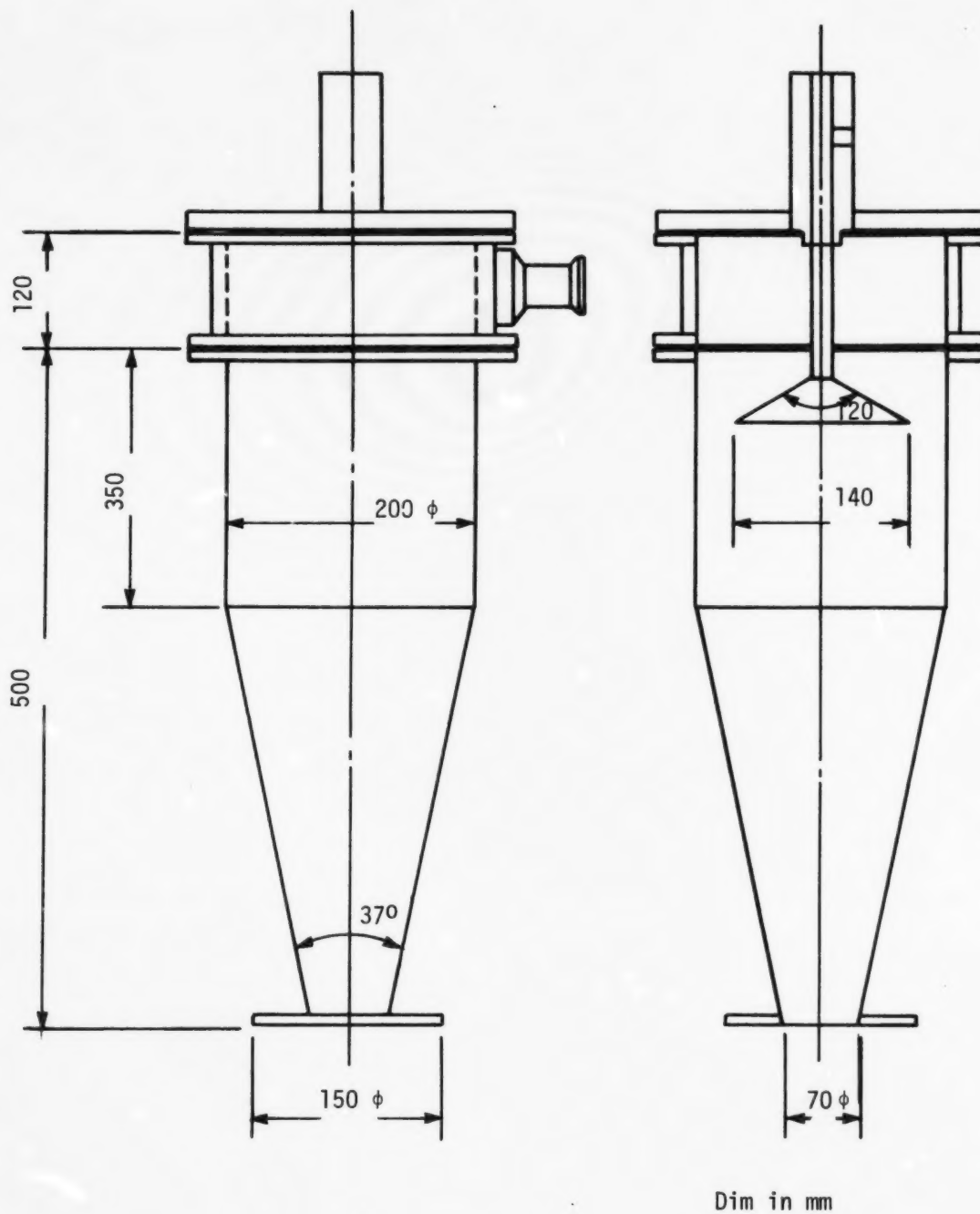


Figure 4.4 Schematic of the stainless steel spouted bed reactor used for the coke gasification

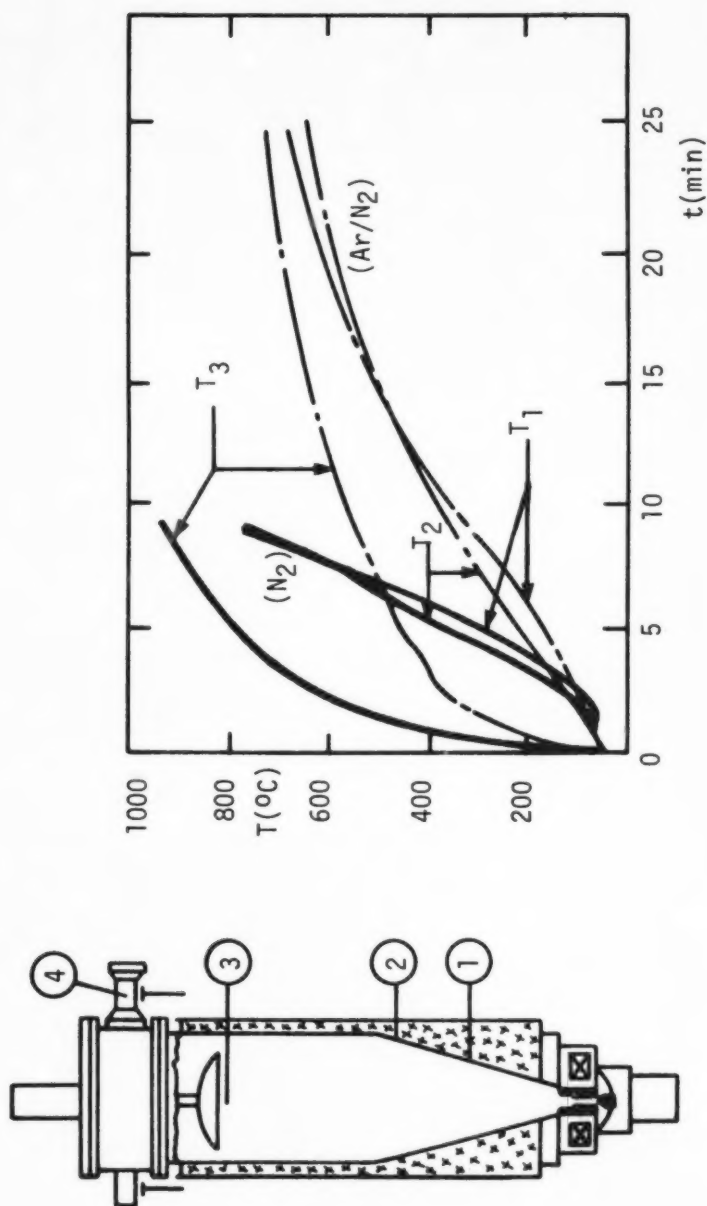


Figure 4.5 Thermal characteristic of the hot-wall reactor
Experimental conditions

Plasma gas	(λ/min)	100(Ar-N ₂)	100(N ₂)
voltage	(V)	28.0	64.0
current	(A)	250.0	245.0
powder	(kW)	7.0	15.7
off-gas temp., T_4	($^{\circ}\text{C}$)	80.0	50.0

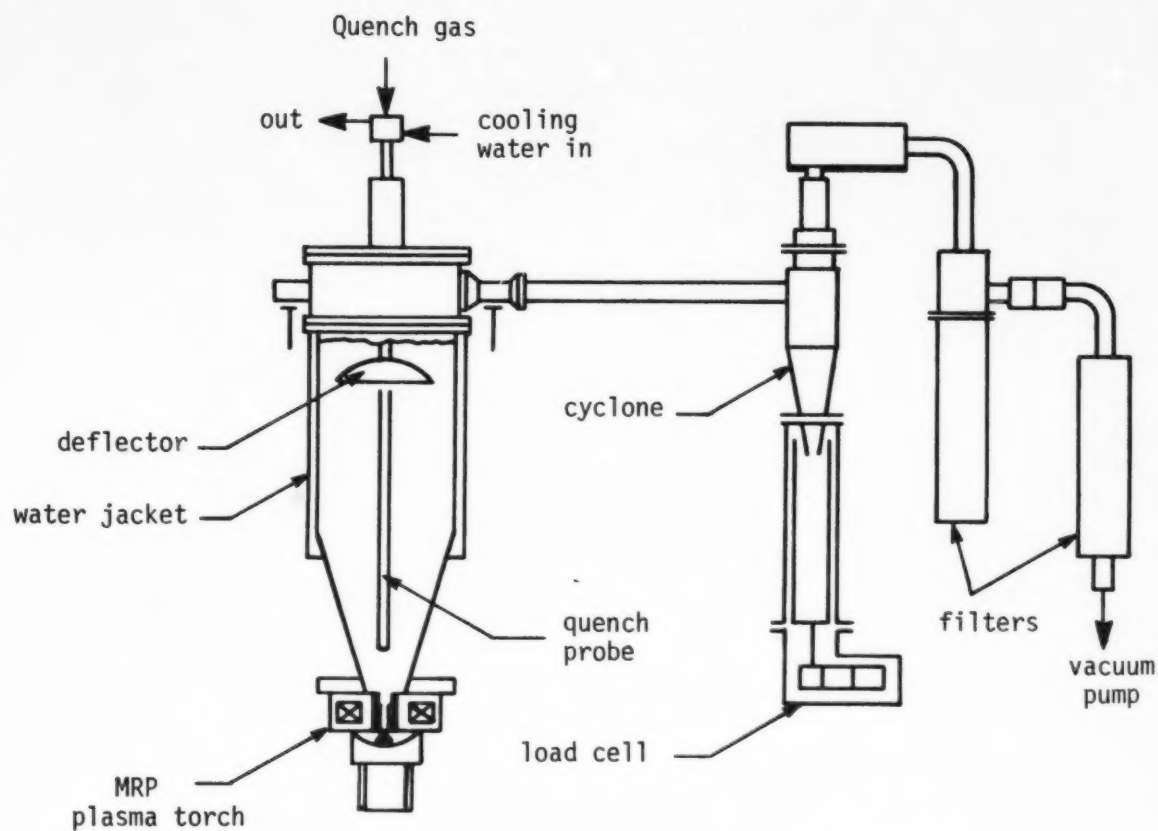


Figure 4.6 The experimental set-up used with the cold-wall spouted bed reactor

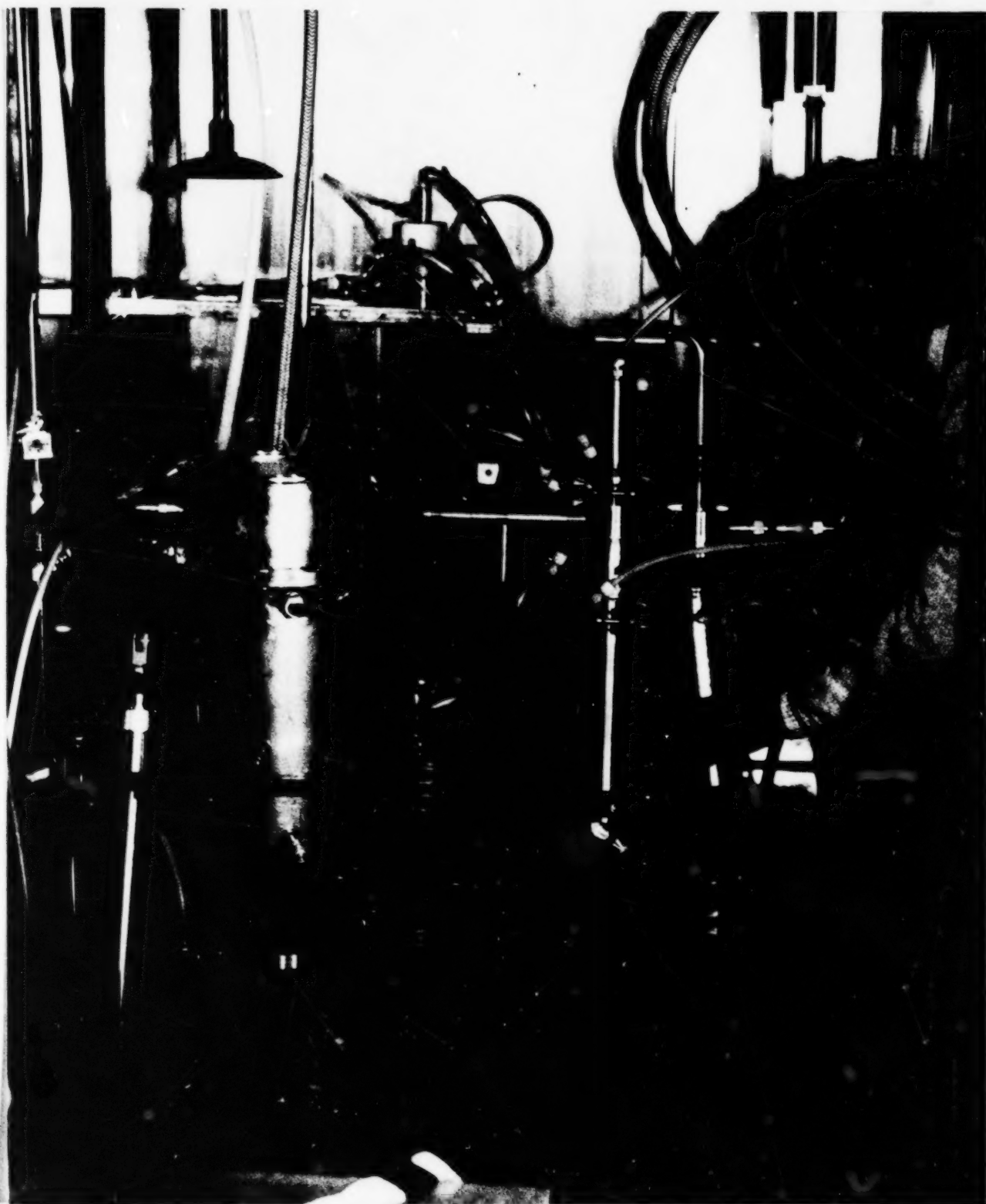


Figure 4.7 Close-up photograph of the water-cooled, stainless steel spouted bed reactor system

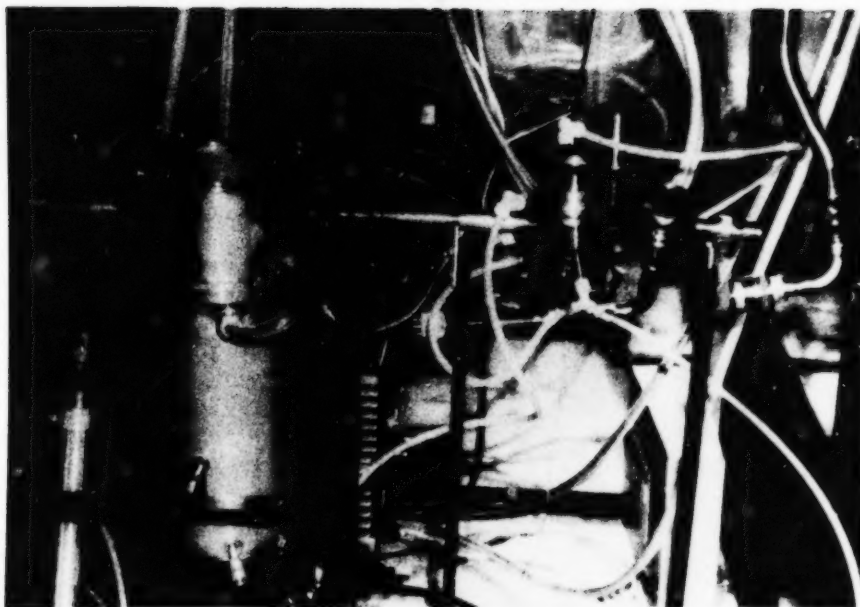


Figure 4.8 Photograph of the experimental set-up

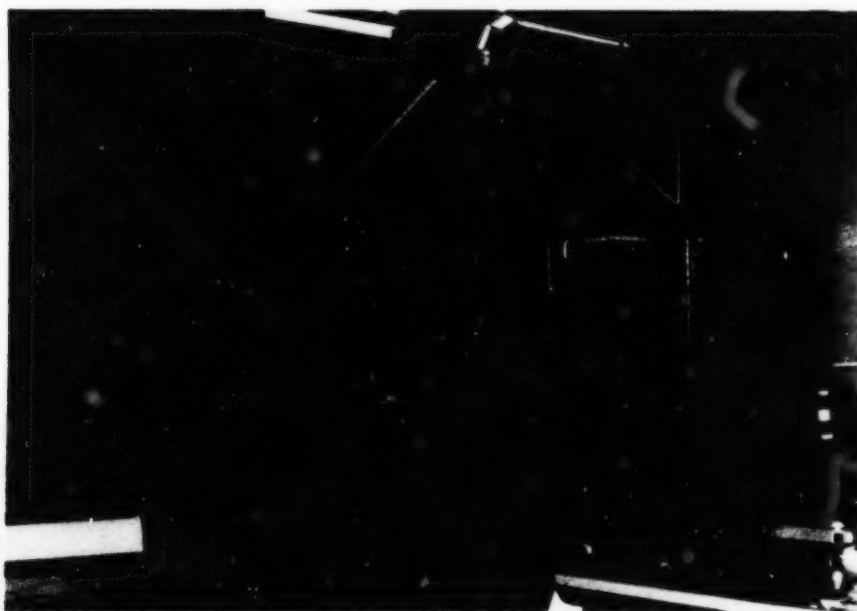


Figure 4.9 Photograph of the experimental set-up



Figure 4.10 Control pannel and date acquisition system



Figure 4.11 Gas chromatograph

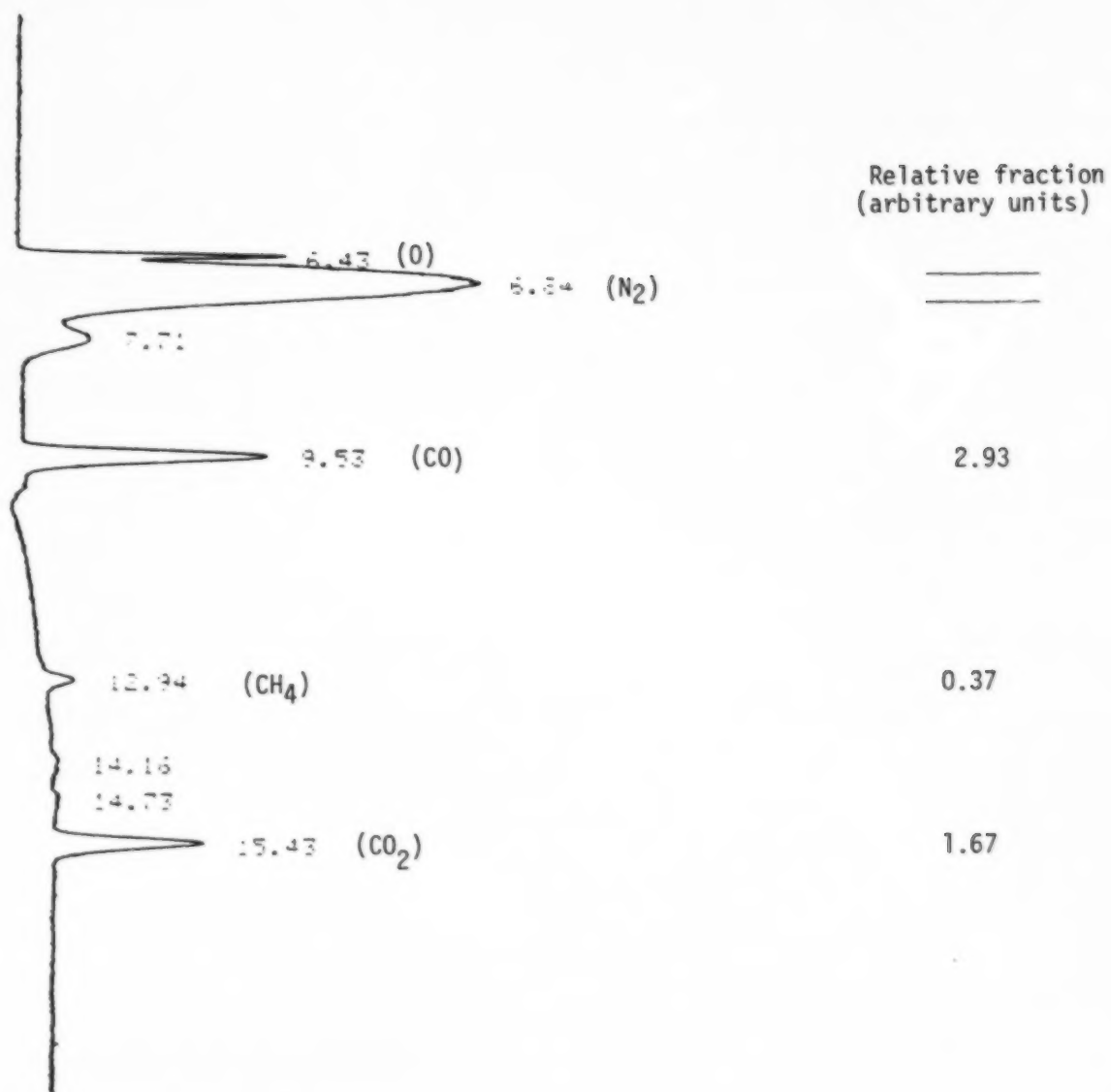


Figure 4.12 Typical chromatogram of a sample of the gases obtained in run #30 taken after 8 min operation

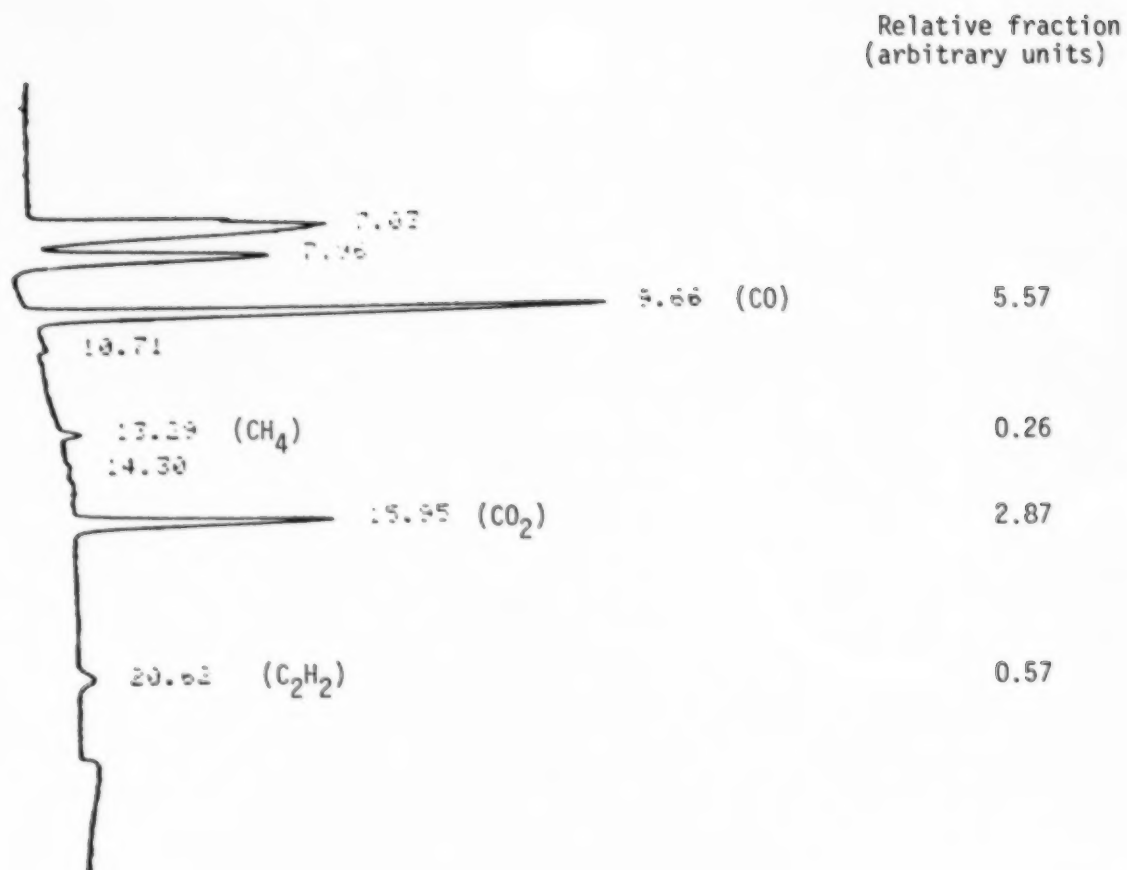


Figure 4.13 Typical chromatogram of a sample of the gases obtained in run #42 taken after 6 min operation

5. Conclusions and recommendations for further work

A feasibility study was carried out of the gasification of petroleum coke using plasma technology. Throughout its two-year period, the project went through the following three stages of development; the first stage was devoted to the design and the testing of the magnetically rotated plasma torch (MRP-Torch) which was successfully operated with pure hydrogen as well as different argon-hydrogen mixtures at power levels varying between 10 and 30 kW. Systematic calorimetric study showed that the torch energy efficiency, which was typically between 80 and 90%, depends on the plasma gas flow rate and the relative position of the magnetic coil with respect to the anode. Torch energy efficiencies as high as 94% were reported in some of the runs.

The second stages of this study was mainly concerned with the development and the testing of the plasma spouted bed reactor. While the concept of such a reactor has been previously used in coal-gasification studies, very little was known about its performance and design criteria. This type of reactor revealed itself as being most interesting due to its high energy efficiency, long residence time and the repeated exposure of the solids to be treated to the plasma.

The last stage of this work dealt with the study of the gasification of fluid bed petroleum coke using the plasma spouted bed reactor operated at atmospheric pressure with an argon-hydrogen plasma at a power level in the range of 10-20 kW. The results, however, were rather disappointing since very little gaseous hydrocarbons could be detected at the exit of the reactor. While this could be attributed to the lack of appropriate product quench, it should be underlined that in contrast to other carbonaceous materials used in earlier gasification studies using plasma technology, the petroleum coke had particularly low volatile matter content which could account for the observed difficulty of gasifying any of its constituents.

Based on the above observations, it is unlikely that further work on the gasification of petroleum coke using a hydrogen plasma could be successful. A number of interesting options, however, are possible and worthy of investigation. Particularly promising is the gasification of the coke as a syngas through the reaction of water vapour with the coke in the plasma spouted bed reactor. The combustion of the petroleum coke in a plasma spouted bed reactor could also offer another interesting technique for the efficient and economical use of this rather inert material.

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